Indian J. Phys. **67A** (4), 357 – 361 (1993)

NOTE

Theoretical prediction of elastic constants of solid solutions of alkali halides

Anit Kumar Giri*
MLS Professor's Laboratory, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-700 032, India

Received 22 December 1992, accepted 12 March 1993

Abstract : Using some simple well known expressions, the three independent elastic constants C_{11}, C_{12} and C_{44} of solid solutions of alkali halides have been expressed in terms of those of the constituent alkali halides, their molecular fractions and lattice constants. The values obtained for C_{11}, C_{12} and C_{44} are in nice agreement with the experimental values for NaCl-NaBr, KCl-KBr and KBr-KI systems

Keywords Elastic constants, alkali halides, Debye temperatures, bulk moduli, force constants

PACS Nos. : 62.20.Dc, 63.70.+h

In view of much importance of solid solutions of alkali halides, theoretical prediction of its different physical properties has attracted much attention ([1] and references therein). Elastic constants of solid solutions of alkali halides are important parameters from which bulk modulus, Young's modulus, Poisson's ratio, etc. can be calculated. Using different models for different potential functions, elastic constants of solid solutions of alkali halides have been calculated by many authors ([2] and references therein) yielding different values with different order of agreement with experimental data. In this communication, an attempt has been made to derive expressions for the three single crystal elastic constants C_{11}, C_{12} and C_{44} of solid solutions of alkali halides in terms of those of the constituent alkali halides and other physical parameters using some simple well-known relationships. We begin with the well known Vegard's law [3] given by

$$a = xa_1 + ya_2 \tag{1}$$

where a is the lattice constant of the solid solution of the constituent alkali halide compounds 1 and 2 combined in the molecular proportion $x : y$ so that $x+y = 1$ having lattice constant a_1 and a_2 respectively. Although eq. (1) is an emperical one, its validity for the case of solid solutions of alkali halide crystals have been successfully tested by many authors [4–8].

* Present address : Institut de Ciencia de Materiales, C. S. I. C., Serrano 144, 28006 Madrid, Spain.

Differentiating eq. (1) with respect to pressure P, we write,

$$\frac{da}{dP} = x\frac{da_1}{dP} + y\frac{da_2}{dP}. \tag{2}$$

Now, the volume V for cubic materials is given by $V = ta^3$ (t is a factor involving the symmetry of the crystal and is constant for a given crystal type like *fcc* or *bcc* etc.) and compressibility K by $K = -\frac{1}{V}\frac{dV}{dP}$, we have

$$\frac{da}{dP} = -\frac{aK}{3}. \tag{3}$$

Substitution of eq. (3) in eq. (2) yields,

$$aK = xa_1K_1 + ya_2K_2, \tag{4}$$

where K, K_1 and K_2 are the compressibilities of the solid solution, compound 1 and compound 2 respectively.

The compressibility K of a material of atomic/molecular weight M and density ρ is related to the Debye temperature θ through the relation [9]

$$K = \frac{A}{\theta^2 M^{2/3}\rho^{1/3} f^{1/3}}, \tag{5}$$

where A is the constant and f is a function of Poisson's ratio, ν, given by

$$f = \frac{1+\nu}{3(1-\nu)} + \frac{4(1+\nu)}{3(1-2\nu)}.$$

The value of Poisson's ratio is nearly the same for all the alkali halide crystals and for all practical purposes we consider f to be constant. Now substitution of eq. (5) in (4) and again writing for cubic materials $V = t\,a^3$, gives

$$a^2M^{-1}\theta^{-2} = a_1^2M_1^{-1}\theta_1^{-1} + ya_2^2M_2^{-1}\theta_2^{-1} \tag{6}$$

where $M = xM_1 + yM_2$, M_1 and M_2 are the molecular weight of the solid solution having Debye temperature θ, compound 1 having Debye temperature θ_1 and compound 2 having Debye temperature θ_2 respectively.

Now, to derive expressions for the elastic constants of the solid solutions of alkali halides we make use of the relationship connecting the nearest neighbour control force constant α to Debye temperature given by [10]

$$\alpha = uM\theta^2 \tag{7}$$

where u is a constant for a particular type of lattice *i.e.* it has the same value for, say, *fcc* lattice. If we assume that the next nearest neighbour central force constant β and nearest neighbour angular force constant γ obey the same type of relationship like eq. (7) with different values of constants, we may write

$$\beta = vM\theta^2 \tag{8}$$

$$\gamma = wM\theta^2. \tag{9}$$

The three independent single crystal elastic constants C_{11}, C_{12} and C_{44} are related to the force constants α, β and γ through the expressions [11],

$$aC_{11} = 2\alpha + 4\beta + 2\gamma, \tag{10}$$

$$aC_{12} = \alpha - 5\gamma, \tag{11}$$

$$aC_{44} = \alpha + 3\gamma, \tag{12}$$

for *fcc* lattice.

From eqs. (7) – (9) we may write,

$$aC_{11} = TM\theta^2 \tag{13}$$

where $T = 2u + 4v + 2w$ has the same value for the solid solution as well as the compounds since all those for alkali halides have *fcc* structure. Now writing $M\theta^2 = aC_{11}/T$ from eq. (13) substituting in eq. (6) gives,

$$aC_{11}^{-1} = xa_1C_{11}'^{-1} + ya_2C_{11}''^{-1} \tag{14}$$

C_{11} is the elastic constant of the solid solution and prime (′) and double prime (″) refers to C_{11} for compounds 1 and 2 respectively. Again using eqs. (7), (8), (9) and (11) and (7), (8), (9) and (12) we obtain the similar expressions as eq. (14) for C_{12} and C_{44} given by

$$aC_{12}^{-1} = xa_1C_{12}'^{-1} + ya_2C_{12}''^{-1}, \tag{15}$$

$$aC_{44}^{-1} = xa_1C_{44}'^{-1} + ya_2C_{44}''^{-1}. \tag{16}$$

Eqs (14), (15) and (16) represent the expressions for the elastic constants C_{11}, C_{12} and C_{44} of the solid solutions of alkali halide compounds in terms of those of the constituent alkali halides, their molar fractions and lattice constants. All these values for the alkali halides are known. Hence, the elastic constants may be calculated for the solid solutions at any concentration of the components.

Table 1 shows the values of C_{11}, C_{12} and C_{44} for the solid solutions of NaCl-NaBr, KCl-KBr and KBr-KI systems calculated using eqs. (14), (15) and (16) alongwith their respective experimental values. The values of lattice constants of the constituents are taken from Tosi [12]. The agreement between the calculated and experimental values are excellent. This shows the validity of the expressions for elastic constants of the solid solutions of alkali halides derived in this communication.

Acknowledgments

The author avail himself of this opportunity to thank his Professors G B Mitra and D Chakravorty for their help in many ways. The author also acknowledges the research associateship granted by a project supported by the National Science Foundation, Washington, D C, through Special Foreign Currency Programme.

Table 1. Elastic constants of solid solutions of alkali halides.

System	Molecular fraction (%)	Elastic constant* (10^{11} dynes/cm^2)					
		C_{11}		C_{12}		C_{44}	
		Calc.	Expt.	Calc.	Expt.	Calc.	Expt.
	100 NaCl	–	4.585	–	1.264	–	1.265
	90 NaCl	4.473	4.497	1 240	1.244	1.229	1.238
	83 NaCl	4.398	4.435	1.224	1.230	1.205	1.218
	74 NaCl	4.307	4.356	1.203	1.213	1 176	1.194
	64 NaCl	4.211	4.268	1 182	1.193	1.146	1 166
	54 NaCl	4.120	4.180	1 162	1 173	1.118	1.139
NaCl–NaBr	45 NaCl	4 042	4.100	1.144	1 155	1.094	1 114
	30 NaCl	3.921	3.968	1.116	1.125	1.056	1.073
	17 NaCl	3.823	3.854	1.094	1.100	1.026	1.037
	100 NaBr	–	3.704	–	1 066	–	0 990
	100 KCl	–	3.838	–	0.683	–	0.633
	94 KCl	3.796	3.804	0.674	0.676	0.623	0.625
	87 KCl	3 749	3.763	0 664	0.668	0.612	0.616
	62 KCl	3.591	3.620	0.631	0.638	0.575	0.584
KCl–KBr	46 KCl	3.498	3.528	0.612	0.619	0.555	0.563
	39 KCl	3 459	3.487	0.604	0.610	0.546	0.554
	29 KCl	3 406	3 430	0.593	0.599	0 535	0 541
	15 KCl	3 335	3 349	0.579	0.582	0.519	* 0 523
	100 KBr	–	3 263	–	0 564	–	0.504
	100 KBr	–	3 263	–	0.564	–	0 514
	90 KBr	3.173	3 194	0.550	0.553	0 485	0 491
	85 KBr	3.131	3.160	0.543	0.548	0 476	0.484
	78 KBr	3.073	3 112	0.534	0.540	0 465	0.475
KBr–KI	71 KBr	3.018	3.064	0.526	0.532	0.454	0.465
	60 KBr	2.937	2 989	0.513	0.520	0.438	0.450
	52 KBr	2.882	2.934	0.504	0.512	0.427	0.440
	40 KBr	2.803	2.851	0.491	0.499	0.412	0.424
	20 KBr	2.684	2.714	0.472	0.477	0.390	0 397
	10 KBr	2.629	2.646	0.463	0.466	0.380	0.383
	100 KI	–	2.577	0.455	0.455	–	0.370

* The experimental values are taken from Srivastava [13].

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